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**STUDIES OF THE BREAKDOWN MECHANISM
OF POLYMERS**

**VII The Thermal Decomposition of a
Polyhydrazide and of Polyoxadiazoles**

GERHARD F. L. EHLERS

KURT R. FISCH

WILBERT R. POWELL

TECHNICAL REPORT AFML-TR-72-67

APRIL 1972

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. G. F. L. Ehlers (AFML/LNP) as Project Engineer.

This report covers work conducted from April 1970 to November 1970.

The authors wish to thank G. L. Burkett, University of Dayton Research Institute, Dayton, Ohio, for the synthesis of the polymers used in this study, L. D. Smithson for the high resolution mass spectra of the sublimates and Mary T. Ryan for the nuclear magnetic resonance study of one of the sublimates. Elemental analyses were performed by the Analytical Branch, Air Force Materials Laboratory.

This report was submitted by the authors in December 1971, has been reviewed and is approved.



R. L. VAN DEUSEN
Chief, Polymer Branch
Nonmetallic Materials Division
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ABSTRACT

Poly-1,3-phenylene hydrazide, when heated to 250°C in vacuum, partially undergoes cleavage of the N-N bond to yield isophthalonitrile, water, carbon monoxide, and carbon dioxide. The major part converts to the corresponding polyoxadiazole.

Poly-1,3- and -1,4-phenylene -2,5(1,3,4-oxadiazole) decompose essentially in the 450 to 500°C region to yield isophthalonitrile (also p-aminobenzonitrile in the case of the 1,4-polymer), nitrogen, carbon dioxide, hydrogen cyanide, carbon monoxide, water, ammonia, methane, and hydrogen. The 1,4-polymer decomposes at a slightly higher temperature than the 1,3-polymer and forms less gaseous products and more condensate. The oxadiazole ring degrades before the benzene ring. Initial competing reactions seem to be the removal of nitrogen, further degradation of the remaining ether linkage, and the elimination of oxygen with subsequent cleavage of the residual -C=N-N=C- linkage.

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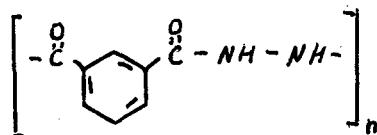
SECTION I

INTRODUCTION

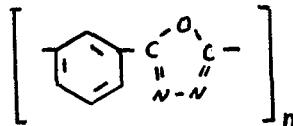
This work is a continuation of studies of the thermal breakdown mechanism of aromatic-heterocyclic polymers. Previous work has been described in the Technical Reports AFML-TR-67-89, -67-295, -67-428, -68-289, -70-63, and -71-116.

This report describes the decomposition of the following polymers:

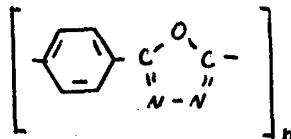
1. Poly-1,3-phenylene hydrazide



2. Poly-1,3-phenylene-2,5-(1,3,4-oxadiazole)



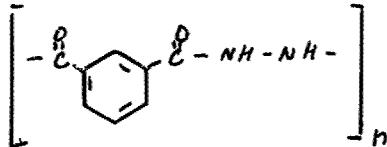
3. Poly-1,4-phenylene-2,5-(1,3,4-oxadiazole)



The polymers were decomposed stepwise in vacuum at three different temperatures between 250 and 600°C and the gases analyzed by mass spectroscopy. Residues and sublimates were subjected to elemental analysis, and infrared spectroscopy; high resolution mass spectroscopy and nuclear magnetic resonance were used to elucidate the structure of sublimates.

SECTION II

DISCUSSION

1. Poly-1,3-phenylene hydrazide

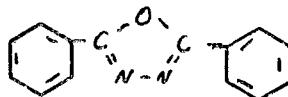
Polyphenylene hydrazide was included in this study, since it is a prepolymer of poly-1,3-phenylene-2,5-(1,3,4-oxadiazole) discussed below.

Frazer and Wallenberger (Reference 1) converted this polyhydrazide to the polyoxadiazole by heating it for 30 to 72 hours at 280°C in vacuum.

The polymer used in this study was prepared in our laboratory from isophthaloylhydrazide and isophthaloylchloride in hexamethylphosphoramide at 5-10°C, according to the procedure of Frazer and Wallenberger (Reference 2); the isophthaloylhydrazide was synthesized from dimethylisophthalate and hydrazine in methanol (Reference 3). Fractions of this polymer, with viscosities from 0.7 to 1.3 (0.3% in DMSO) were dissolved in DMSO, precipitated in a Waring blender with methanol, Soxhlet-extracted with methanol, washed with boiling hexane, and vacuum dried for 16 hours at 118°C and 0.1mm.

The TGA curve (Figure 1) seems to confirm that the first step of the thermal breakdown in the solid state (around 300°C) consists of the loss of water (theory: 10%) and the conversion to the polyoxadiazole. The data in Table I indicate, however, that the mechanism is more complex. Only a total of 2.8% of water was detected in the decomposition study, and a sublimate is the major decomposition product at the lower temperatures. The major

component of this sublimate appears to be isophthalonitrile. Melting point of the major fraction, in the form of colorless crystals, was 141°C (isophthalonitrile 162-163°C, mixed melting point 156-159°C). Its IR spectrum is very similar to that of isophthalonitrile (Figure 2), and its NMR spectrum indicates an AB₂C system, typical of a meta substituted benzene with both substituents being the same. Largest peak of the mass spectrum of the sublimate is m/e 128, which corresponds to isophthalonitrile. Other peaks suggest the presence of fragments, such as

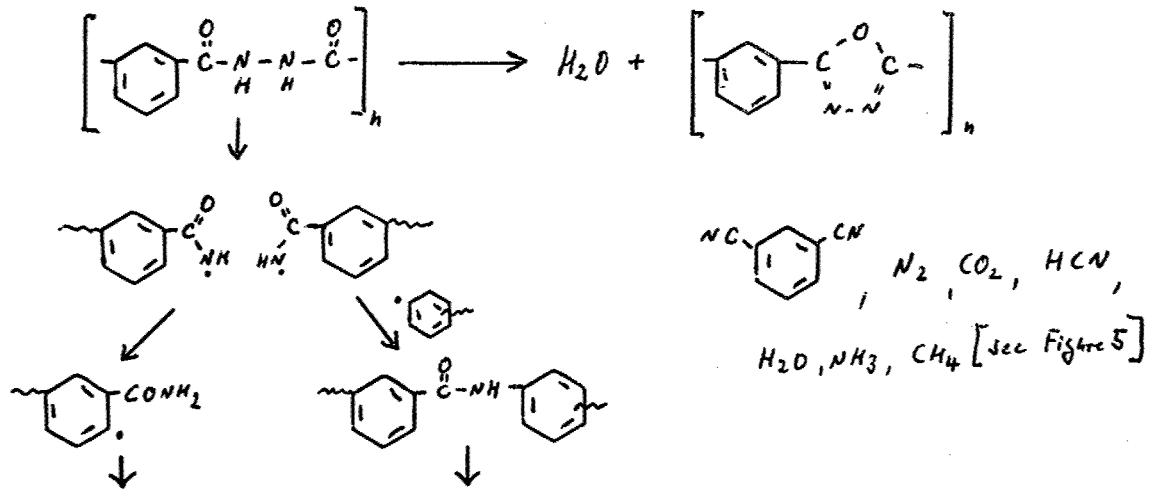


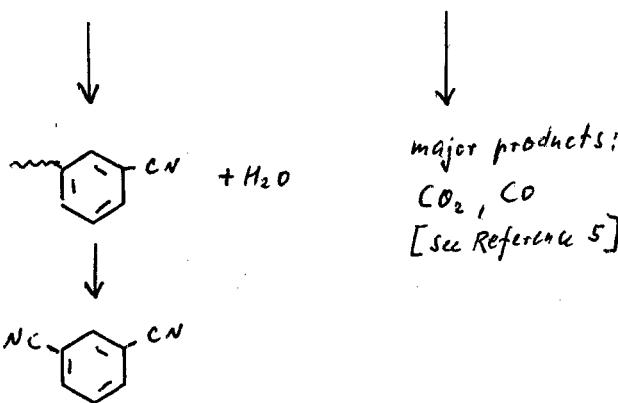
The residues formed during the decomposition are very hygroscopic. Their infrared spectra are shown in Figure 3; the spectrum of the 600°C residue was featureless because of extensive crosslinking and was omitted. The spectrum of the 250°C residue is very similar to that of poly-1,3-phenylene-2,5-(1,3,4-oxadiazole) (Figure 4). The disappearance of the NH stretching at 3300 cm⁻¹ and the emergence of a broad NH-absorption around 3500 cm⁻¹ may be the result of the disappearance of the hydrazide linkage and the formation of amide linkages and free amide groups (see mechanism below). Bands characteristic of the oxadiazole unit are the =C-O-C= stretching modes at 1070 and 960 cm⁻¹ (Reference 4). Other bands which seem to be characteristic of the polyoxadiazole are at 815, 785, 720, and 680 cm⁻¹. The spectrum of the 400°C residue is similar to that of the 250°C residue, but more diffuse as the result of crosslinking, and has an additional band at 2250 cm⁻¹, possibly the C≡N stretching vibration.

In contrast to the relatively small (0.25 mole) amount of water, 0.53 mole per polymer unit of carbon dioxide and 0.39 mole per polymer unit of nitrogen are being produced. This would indicate that these products must have formed partially from the polyhydrazide directly and through mechanisms which do not involve formation of water. It is suggested that carbon dioxide results from intermediate amide linkages via isocyanate-carbodiimide groups, as described before for polyamides (Reference 5). More difficult to explain is the formation of nitrogen without concomitant production of water. It is possible, however, that some water condensed in the apparatus and went undetected.

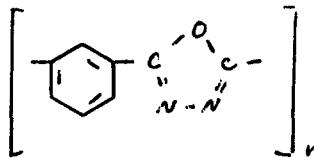
Other volatiles of significance, in addition to carbon dioxide, water, and nitrogen, are carbon monoxide, hydrogen cyanide, ammonia, and hydrogen, the last three mainly being formed at the highest temperature step. At this temperature, the decomposition of the intermediate polyoxadiazole leads to the formation of carbon monoxide, while the benzene rings supply the hydrogen. This hydrogen reacts partially with nitrogen and cyanogen from the oxadiazole ring to yield hydrogen cyanide and ammonia.

The following schematic depicts the principal features of the suggested overall mechanism:





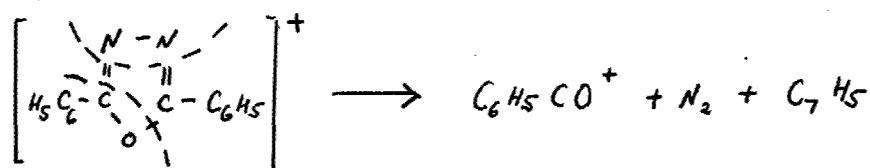
2. Poly-1,3-phenylene-2,5-(1,3,4-oxadiazole)



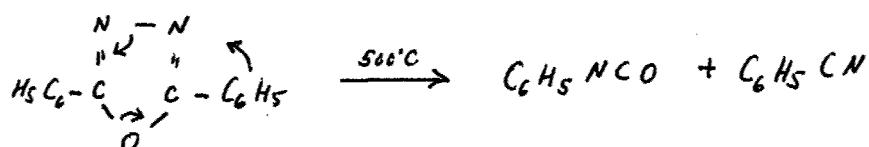
This polymer was prepared by a modification of a procedure by Iwakura and coworkers (Reference 6). These authors used hydrazine sulfate as one of the components, while our polymer had been prepared from hydrazine hydrochloride and isophthalic acid by heating these components in polyphosphoric acid for 16 hours at 180°C. The polymer had an inherent viscosity of 0.47 dl/g in conc. sulfuric acid. The analysis can be found in Table II.

Some previous work has been reported on the thermal degradation of polyoxadiazoles. Cotter and coworkers (Reference 7) studied the thermal decomposition of a m,p-polyoxadiazole from diethylterephthalate, isophthaloylchloride, and hydrazine hydrate and found that the thermal breakdown mechanism of the polymer seems to correspond more to the electron impact breakdown than the thermal breakdown of the model 2,5 diphenyl-1,3,4-oxadiazole:

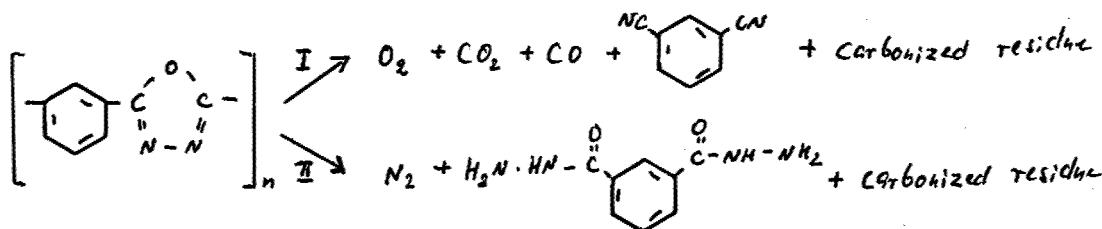
Electron impact breakdown:



Thermal breakdown:



Decomposition of the polymer in sealed, evacuated ampoules at $420-460^\circ\text{C}$ over periods of several hours yielded products containing 32% of the available nitrogen, in addition to carbon monoxide, carbon dioxide, benzene, benzonitrile, and iso- and terephthalonitrile. Rode and Bondarenko (Reference 8.) report the formation of nitrogen, oxygen (in small amounts), carbon dioxide, carbon monoxide, isophthalonitrile, and isophthalohydrazide during the decomposition of poly-1,3-phenylene-2,5-(1,3,4-oxadiazole) at temperatures between 350 and 500°C , and believe that the following two reactions occur, the first being the dominating step:



The authors believe that carbon dioxide results from a secondary reaction of oxygen with carbon monoxide.

Table II presents the results of our decomposition study. A greenish-yellow sublimate formed mainly at 475°C, which accounts for 40% of the total weight loss; thin-layer chromatography was used in an attempt to separate the sublimate into possible components. The two fractions which were separated both showed the spectrum of the previously identified isophthalonitrile, but when subjected to mass spectroscopy, one had a molecular ion peak of $m/e=128$ (isophthalonitrile), while the other had a parent peak at 256 and a weaker peak at 284, in addition to a number of peaks from fragmentation products. The m/e 256 peak would correspond to a dimer of isophthalonitrile. No mass peaks were found which would indicate the presence of isophthalohydrazide.

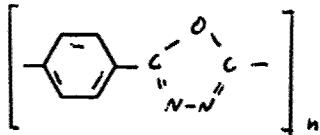
As in previous cases of polymers containing nitrogen and oxygen (References 5 and 9), a major part of the nitrogen is being retained in the residues, but only little oxygen. The infrared spectrum of the 350°C residue (Figure 4) has not changed from that of the original polymer, and the spectrum of the 475°C residue is featureless, with the exception of a C≡N stretching vibration at 2240 cm^{-1} . Nitrogen and carbon dioxide are the major volatile products at the lower temperatures, along with carbon monoxide and water. Hydrogen cyanide and hydrogen are the dominating products at the higher temperature, with some ammonia and methane.

As far as the breakdown mechanism is concerned, we feel that the decomposition of polyoxadiazoles does not occur according to two separate routes as suggested by Rode and Bondarenko. If evolution of carbon monoxide

were the first decomposition step, this would lead either to the formation of nitrile and nitrogen or to a fragment which in turn yields nitrogen. If, on the other hand, nitrogen were the first product of decomposition, an ether linkage would remain which is known (Reference 10) to degrade with formation of carbon monoxide and carbon dioxide. In other words, it is not likely that either nitrogen or oxygenated products form; one is likely to cause the formation of the other.

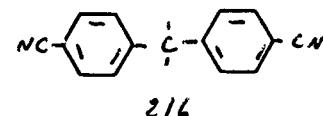
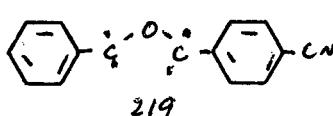
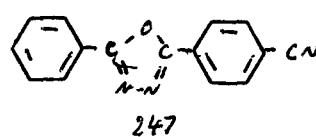
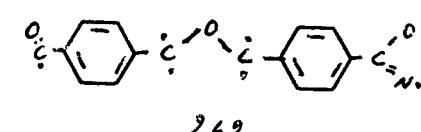
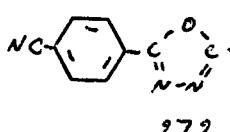
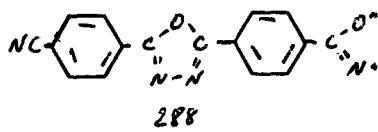
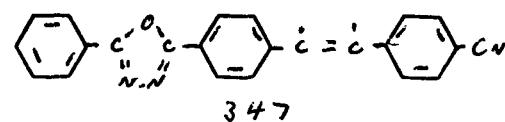
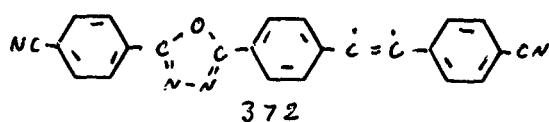
It is suggested that the thermal breakdown of the polymer begins with the decomposition of the oxadiazole ring, which may occur according to routes 1 and 2 of the scheme depicted in Figure 5. Both routes together would account for all of the products found, namely isophthalonitrile and (in order of decreasing number of moles per polymer unit) nitrogen, carbon dioxide, hydrogen cyanide, carbon monoxide, water, ammonia, methane, and hydrogen. The formation of carbon dioxide during the decomposition of an ether linkage has been explained before (Reference 10). The postulated formation of oxygen and subsequent formation of water with hydrogen from the aromatic ring would explain the presence of water at the higher temperatures. Methane and hydrogen result from the decomposition of the aromatic ring, with some of the hydrogen participating in the formation of hydrogen cyanide and ammonia, and water at the higher temperatures.

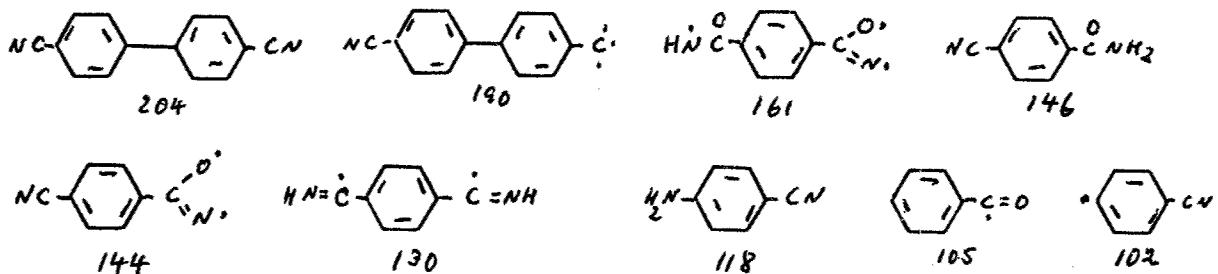
3. Poly-1,4-phenylene-2,5-(1,3,4-oxadiazole)



The polymer was prepared by modifying a procedure by Iwakura and coworkers (Reference 6), as mentioned in the discussion of the poly-oxadiazole. Terephthalic acid and hydrazine dihydrochloride in 50% excess were heated in polyphosphoric acid for 8 hours at 180°C, postheated for 24 hours at 325°C, reprecipitated from methanesulfonic acid into methanol, and Soxhlet-extracted with methanol. The inherent viscosity in methanesulfonic acid was 0.74 dl/g.

Table III shows that a sublimate forms at all three temperature steps, and that the sublimate is the major decomposition product (44.5% vs 2.3% for the gaseous products). A smaller part of it condenses in the center region of the decomposition cell, and is probably of higher molecular weight than the major product in the top part of the cell. It does not seem to melt below its decomposition. Its IR spectrum is shown under 2 in Figure 6; it has the C≡N absorption, but is not identical to terephthalonitrile. Mass spectral analysis of the compound yields a variety of m/e peaks, namely 372, 347, 288, 272, 262, 247, 219, 216, 204, 190, 161, 146, 144, 130, 118, 105, and 102 (major peaks are underlined). Possible assignments for these peaks are:

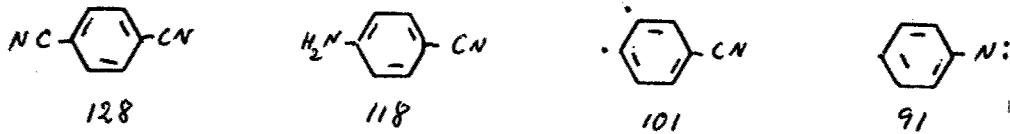




The major part of the sublimate condenses in the top part of the cell.

The yellow product melts between 178 and 198°C. Its mass spectrographic analysis exhibited major peaks at 128 and 118 and minor ones at 101 and 91.

The following assignments can be made:



A large batch of this sublimate was prepared and separated by thin-layer chromatography (methylene chloride) into three compounds. The main fraction, approximately 90% of the total sublimate, was a colorless compound and melted at 234-236°C. Its IR spectrum (1a in Figure 6) was identical to that of terephthalonitrile, which melts at 224-226°C. A smaller, orange fraction melted at 81.5°C (p-aminobenzonitrile: 85.5-86°C). Its IR spectrum (Figure 6 (1b)) was identical to that of p-aminobenzonitrile. The third component consisted of traces of oily products which, from the infrared spectrum, seem to be of aliphatic nature.

The kind of volatiles formed during the decomposition of the poly-p-oxadiazole are the same as for the m-polymer. The fact that the quantity of water formed at 600°C is higher than that at 450°C, indicates that a mechanism for water formation like the one shown in Figure 5 is feasible. The total amount of volatiles from the p-polymer is much smaller than that

from the m-polymer, and the quantity of hydrogen cyanide is relatively large compared to that of carbon monoxide and dioxide. This is confirmed by the analysis of the residue at 600°C, which contains twice the amount of oxygen than does the corresponding residue of the m-polymer. The IR spectra of the residues (Figure 8), when compared with that of the original polymer (Figure 7) show the appearance of the C≡N absorption at 2200 cm⁻¹, and a C=O vibration at 1680 cm⁻¹. Another band emerging at 980 cm⁻¹ may be ascribed to the CH deformation vibration of an aldehyde.

The difference, then, between the decomposition of the p-polymer and that of the m-polymer is as follows: The p-polymer forms less volatiles and more condensibles, consisting of larger fragments and p-aminobenzonitrile in addition to the terephthalonitrile. Less oxygen is removed from the polymers, and an aldehyde or keto group forms in the residues. Traces of aldehyde or ketone may also have formed during the decomposition of the m-polymer; the spectrum of its 350°C residue (Figure 4) contains a shoulder at 1650 cm⁻¹.

The breakdown mechanism for the oxadiazole ring in Figure 5 can, therefore, be supplemented as shown under 1a of the same figure.

SECTION III

EXPERIMENTAL

The apparatus used for the decomposition studies was similar to the one previously described (Reference 10). It consisted of a Quartz test cell (the remainder of the apparatus being Pyrex) fitted with a thermocouple well

and connected to a sample cell, manometer, vacuum pump, and nitrogen inlet. The test cell was heated by means of an aluminum block fitted with two 350W heating cartridges and controlled by an F&M Model-240M Power Proportioning Temperature Programmer. The temperature control was within $\pm 3^{\circ}\text{C}$.

The polymer was dried under vacuum at 110°C overnight and 50-100 mg was weighed into a quartz crucible. The crucible was placed in the test cell and the system was twice evacuated and flushed with nitrogen. The sample cell was degassed by heating with a heat gun. The system was then evacuated to approximately 5μ and the valves closed. The controller was set at the desired temperature, the furnace was turned on, and temperature, time, and pressure were automatically recorded. When no further pressure increase was noted by means of a photoelectric cell and printout, the accumulated gases were permitted to diffuse into the sample cell. The sample cell was removed, a new cell attached, and the system again evacuated and twice flushed with nitrogen. After reestablishing a vacuum of approximately $5-10\mu$ the furnace temperature was raised to the next higher temperature and the procedure repeated. Test temperature selection for obtaining an appropriate amount of pressure was based on information from TGA and from an exploratory run. The final residue was collected and subjected to elemental analysis, weight loss determination, and infrared spectroscopy. Residues for the first two temperature steps were obtained by subjecting two separate samples to the identical history of the original sample up to the first two temperatures, respectively. They were also analyzed as indicated above. The sublimate formed was isolated and examined by infrared spectroscopy, high

resolution mass spectroscopy, and thin-layer chromatography, and in one case by nuclear magnetic resonance.

MASS SPECTROSCOPY OF THE GASES

The gas samples were analyzed in a Consolidated Electrodynamics Corporation Model 21-103B (modified) mass spectrometer. An ionizing voltage of 70 EV and an ionizing current of 10 microamperes was used.

HIGH RESOLUTION MASS SPECTROSCOPY OF THE SUBLIMATES

The sublimates were analyzed in a CEC Model 21-110 mass spectrometer at ionizing voltages of 70 and 15 EV and an accelerating voltage of 8 kv. The samples were introduced via the direct introduction probe at a temperature of 180°^C.

INFRARED SPECTROSCOPY

Infrared spectra were obtained by use of a Perkin-Elmer infrared recording spectrophotometer, model 137, and potassium bromide pellets. The polymers and especially the residues were shaken 1-4 min. in steel vials in a Wig-L-Bug.

THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis was performed in a modified Chevenard thermobalance in nitrogen (flow rate 98 cc/min) at a heating rate of 3°^C/min.

NUCLEAR MAGNETIC RESONANCE

The NMR spectrum of one sublimate was obtained in a Varian A-56/60 spectrometer at 60 Mc/sec at room temperature.

ELEMENTAL ANALYSIS

Elemental analyses were performed by the Analytical Branch, Air Force Materials Laboratory. The data given represent mean values of duplicate runs.

SECTION IV

CONCLUSIONS

Poly-1,3-phenylene hydrazide, upon heating to 250°C in vacuum, partially undergoes cleavage of the N-N bond to form isophthalonitrile and water, as well as carbon monoxide and dioxide, from intermediate amide linkages. The major part of the polyhydrazide cyclizes to form polyoxadiazole, which degrades at the higher temperatures (400 to 600°C) as indicated below.

Poly-1,3-phenylene-2,5-(1,3,4-oxadiazole) yields the same kind of volatiles as the preceding polymer, namely (in order of decreasing molar amounts) isophthalonitrile, nitrogen, carbon dioxide, hydrogen cyanide, carbon monoxide, water, ammonia, methane, and hydrogen. The decomposition occurs, however, at higher temperatures, the amounts of oxygen-containing products are lower and those containing nitrogen are higher. The primary reaction seems to be the elimination of nitrogen from the oxadiazole ring; an ether linkage remains which decomposes to form carbon dioxide and carbon monoxide. A competing reaction, occurring at a somewhat higher temperature, is the removal of oxygen from the oxadiazole ring; it forms water at the higher temperatures with hydrogen from the aromatic ring, and may convert some carbon monoxide to dioxide. The remaining -C=N-N=C- linkage forms nitriles and hydrogen cyanide on further decomposition. Methane and hydrogen form predominantly

at the higher temperatures from the decomposition of the aromatic ring.

Hydrogen contributes to the formation of ammonia from nitrogen.

Poly-1,4-phenylene-2,5-(1,3,4-oxadiazole) undergoes essentially the same breakdown mechanism as poly-1,3-phenylene-2,5-(1,3,4-oxadiazole), but it forms less volatiles and more condensibles such as terephthalonitrile, p-aminobenzonitrile, and larger fragments. The polymer forms less oxygen-containing products, and aldehyde or keto groups are present in the residue at 450°C.

TABLE I

Analyses of Volatiles and Residues of
Poly-1,3-phenylene hydrazide

	C	H	N	O
Analysis calc. for $(C_8H_6N_2O_2)_n$:	59.3	3.7	17.3	19.8
Found for Polymer:	57.0	4.1	16.6	22.9
Found for Residue at 250°C:	65.7	3.1	11.8	
Found for Residue at 400°C:	67.8	3.0	11.7	8.4
Found for Residue at 600°C:	83.8	2.4	11.4	3.2 (2.0 Residue)

Temp. Range °C	Volatile Products (Mole %)							Total Volatiles (Weight %)	Vol & Condensibles (Weight %)*)
	toluene	benzene	CO ₂	CO	N ₂	HCN	H ₂ O		
20-250	traces	—	6.6	1.3	—	0.9	90.2	0.7	0.2
250-400	0.1	—	71.3	3.1	14.5	0.3	10.2	—	0.2
400-600	0.1	0.4	32.2	3.6	40.4	7.0	3.4	5.5	1.5
20-600	0.07	0.2	14.4	0.8	6.8	1.0	2.8	0.5	0.06
20-600	<0.01	0.53	0.05	0.39	0.06	0.25	0.05	0.02	0.05

Volatile Products (Weight %)*)									
Volatile Products (Moles per polymer unit)									
20-600	<0.01	0.53	0.05	0.39	0.06	0.25	0.05	0.02	0.05

*) of starting material

TABLE II
Analyses of Volatiles and Residues of
Poly-1,3-phenylene-2,5-(1,3,4-oxadiazole)

Temp. Range °C	toluene	benzene	Volatile Products (Mole %)						Total			
			CO ₂	CO	N ₂	HCN	H ₂ O	NH ₃				
25-350	0.4	0.1	10.4	2.6	67.8	5.2	10.4	—	1.3	1.8	3.2	
350-475	traces	traces	40.1	11.3	38.4	1.1	7.9	0.5	0.4	0.2	16.6	36.2
475-600	0.1	0.5	3.7	10.0	8.6	27.0	4.0	13.3	4.7	28.0	5.8	5.8
Volatile Products (Weight %)*)												
25-600	0.05	0.1	9.6	2.5	9.8	2.6	1.0	0.8	0.6	0.2	27.2	45.2
Volatile Products (Moles per polymer unit)												
25-600	<0.01	<0.01	0.31	0.13	0.50	0.14	0.08	0.07	0.05	0.01		

*) of starting material

TABLE III

Analyses of Volatiles and Residues of
Poly-1,4-phenylene-2,5-(1,3,4-oxadiazole)

Temp. °C	Volatile Products (Mole %)								Total					
	C ₆ H ₅ CN	C ₆ H ₅ CH ₃	C ₆ H ₆	CO ₂	HCl	N ₂	CO	HCN	H ₂ O	NH ₃	CH ₄	H ₂	Volatiles (Weight %)*	Vol & Condensibles (Weight %)*
25-350	—	—	—	25.6	1.3	47.8	8.1	0.7	12.1	1.1	1.2	2.1	0.2	6.4
350-450	—	—	—	40.2	0.4	50.2	5.6	0.7	1.2	—	0.1	1.6	1.1	28.0
450-600	traces	0.1	0.4	19.3	0.9	7.8	26.7	15.9	1.9	0.9	1.8	24.2	0.8	12.4
Volatile Products (Weight %)*														
25-600	traces	traces	0.01	0.92	0.02	0.80	0.32	0.15	0.03	0.01	0.01	0.02	2.3	46.8
Volatile Products (Moles per Polymer Unit)														
25-600	<0.01	<0.01	<0.01	0.03	<0.01	0.04	0.02	0.08	<0.01	<0.01	<0.01	0.01	0.01	

*) of starting material

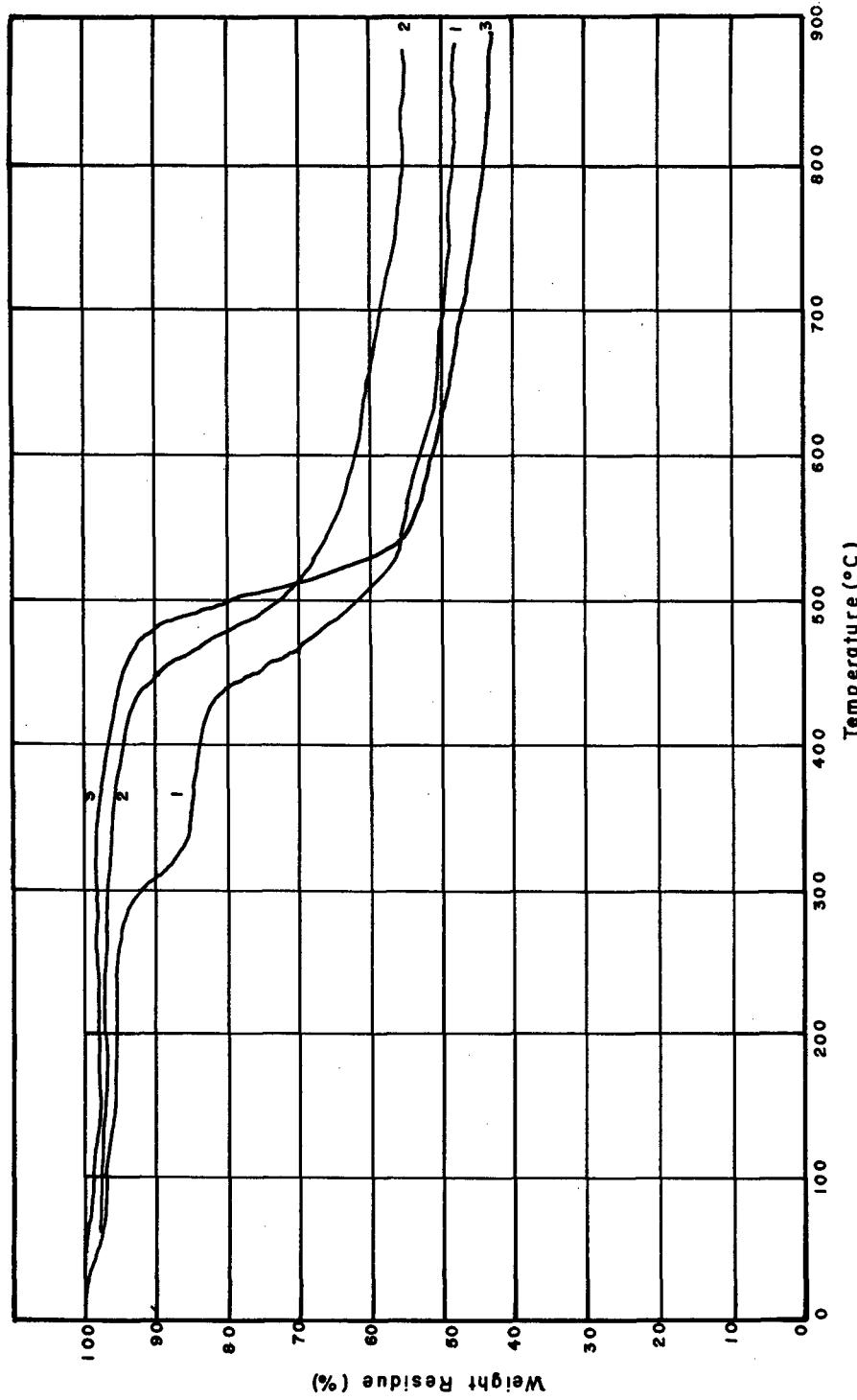


Figure 1. Thermogravimetric Analysis (nitrogen, $\Delta T=180^{\circ}\text{C}/\text{hour}$) of 1: Poly-1,3-phenylene hydrazide, 2: Poly-1,3-phenylene-2,5-(1,3,4-oxadiazole) 3: Poly-1,4-phenylene-2,5-(1,3,4-oxadiazole)

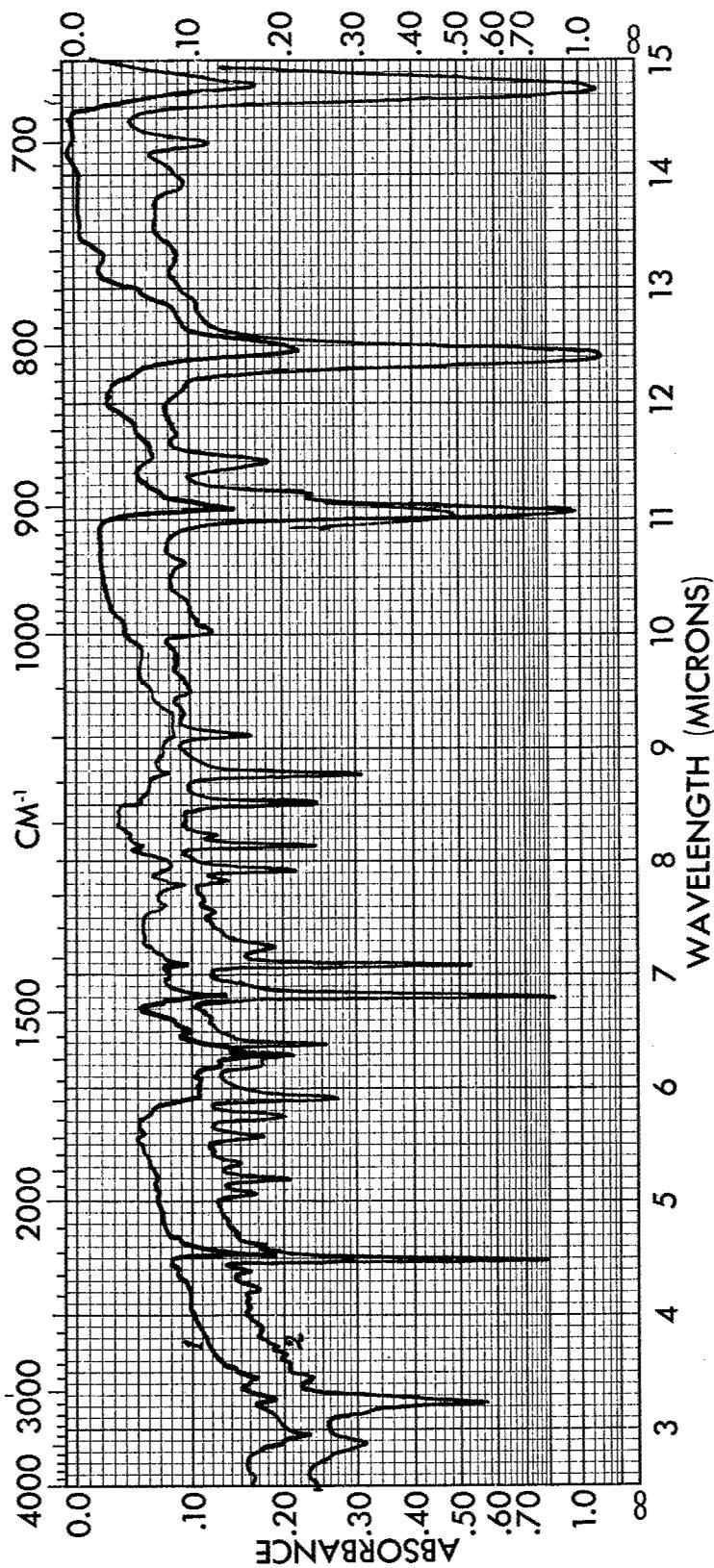


Figure 2. Infrared Spectra of 1: Sublimate of Poly-1,3-phenylene hydrazide 2: Isophthalonitrile

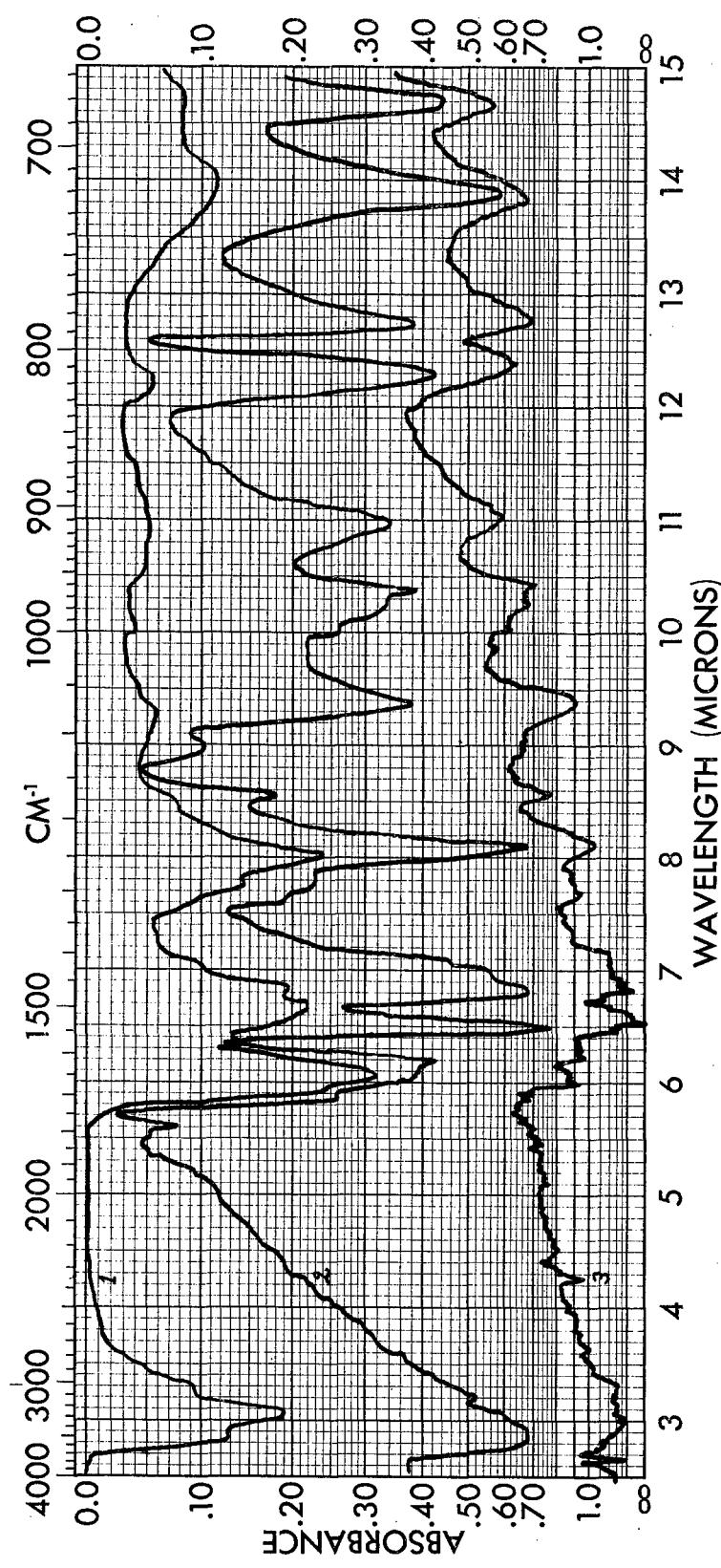


Figure 3. Infrared Spectra of 1: Poly-1,3-phenylene hydrazide 2: Residue at 250°C 3: Residue at 400°C

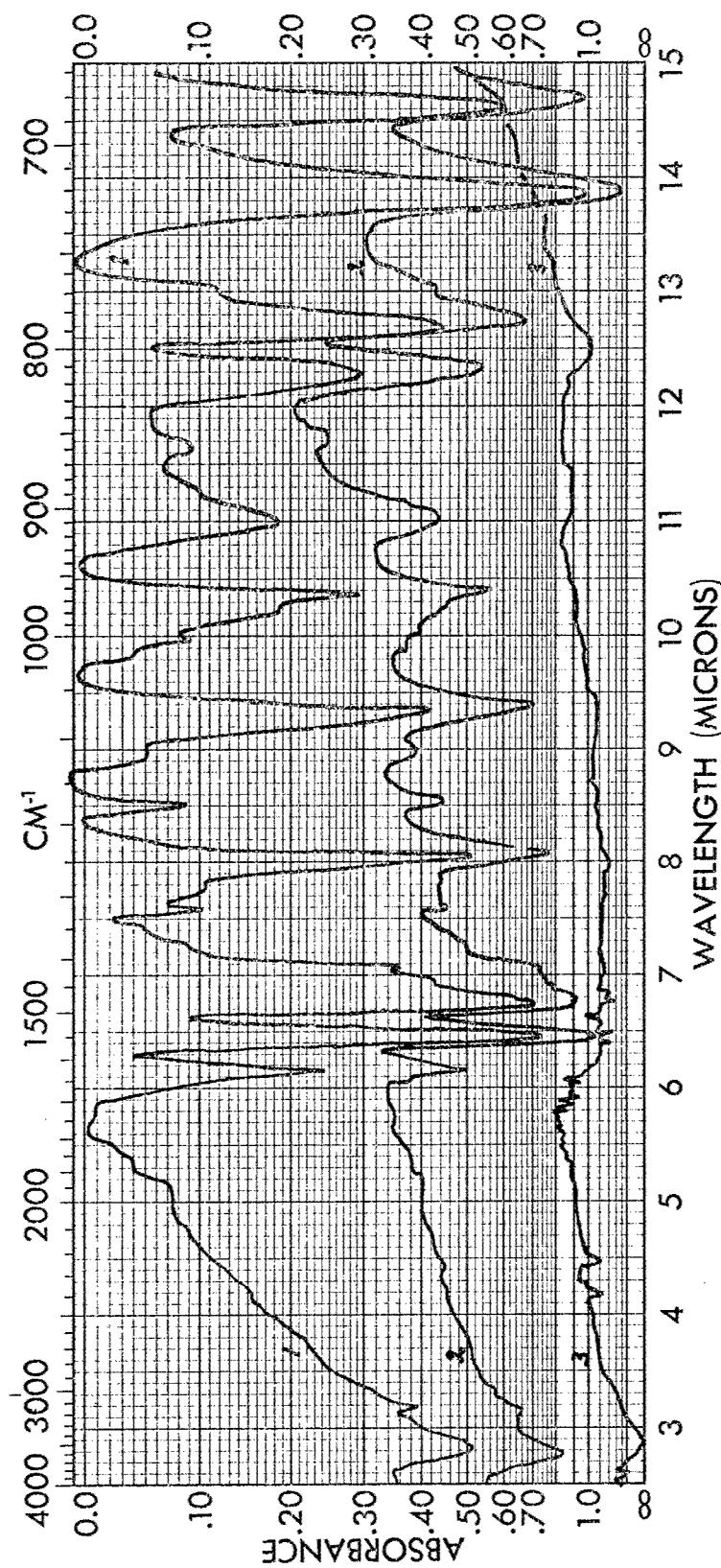
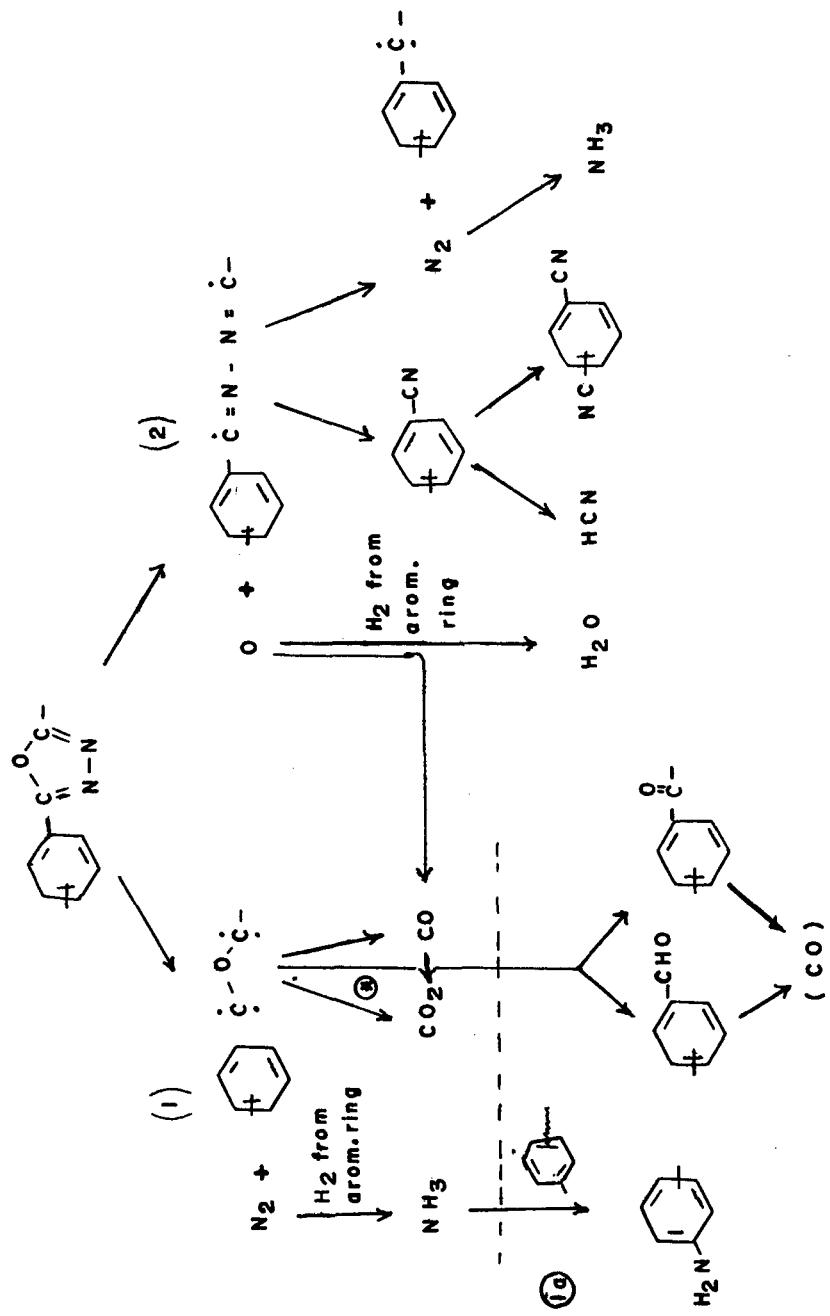


Figure 4. Infrared Spectra of 1: Poly-1,3-phenylene-2,5(1,3,4-oxadiazole); 2: Residue at 350°C; 3: Residue at 475°C



* See Reference 10

Figure 5. Thermal Breakdown Mechanism of the Oxadiazole Ring

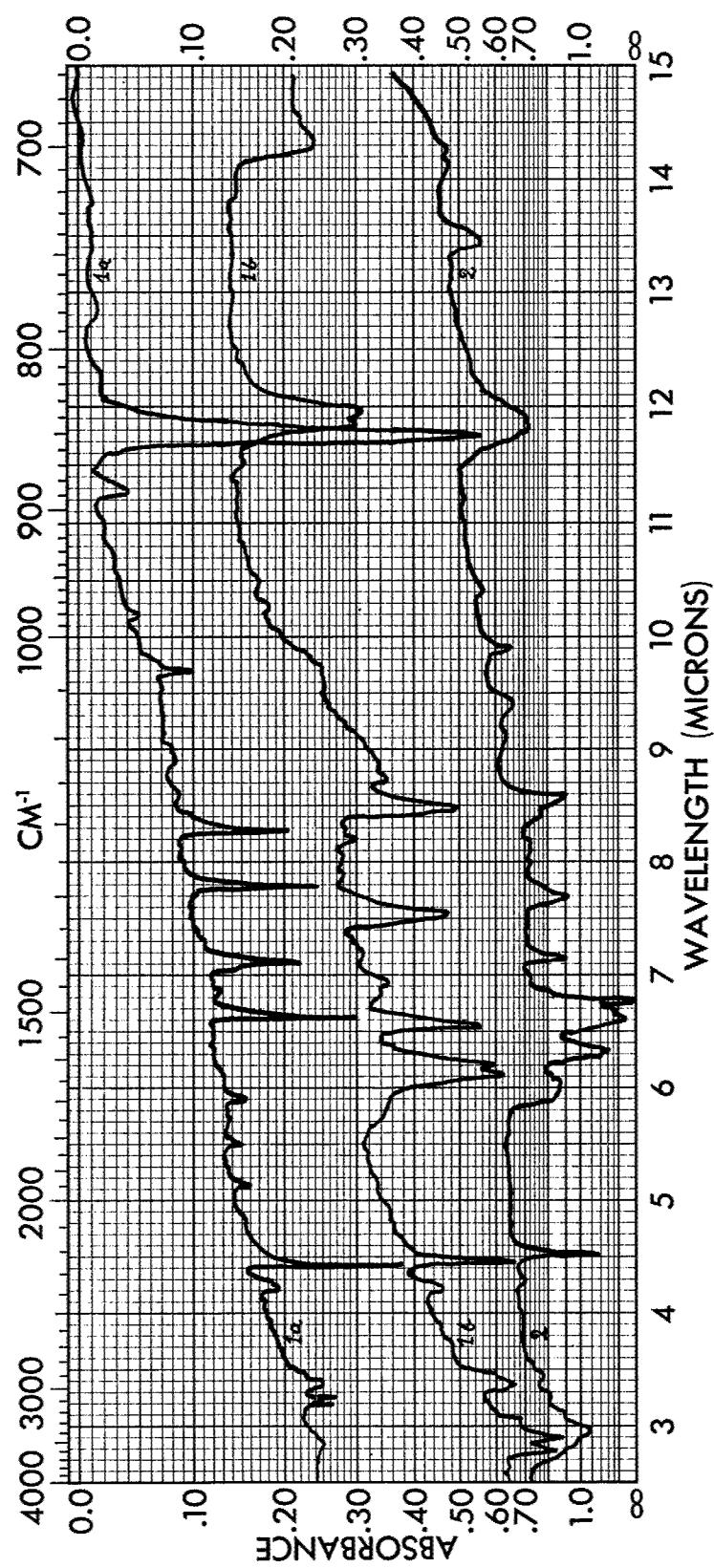


Figure 6. Infrared Spectra of 1a: Major Fraction of the Sublimate of Poly-1,4-phenylene-2,5-(1,3,4-oxadiazole) in the Top Part of the Decomposition Cell; 1b: Minor Fraction in the Top Part; 2: Sublimate in the Center Region of the Decomposition Cell

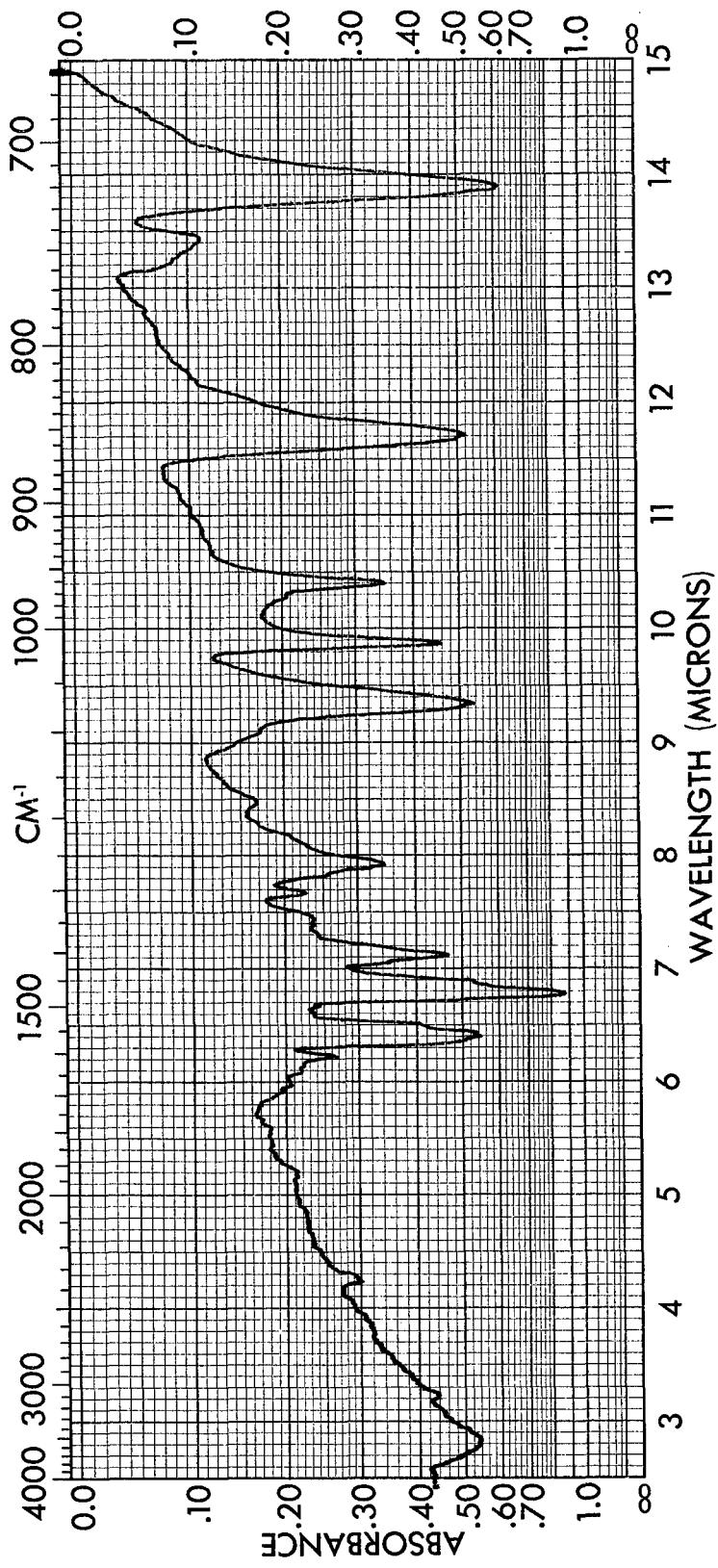


Figure 7. Infrared Spectrum of Poly-1,4-phenylene-2,5-(1,3,4-oxadiazole)

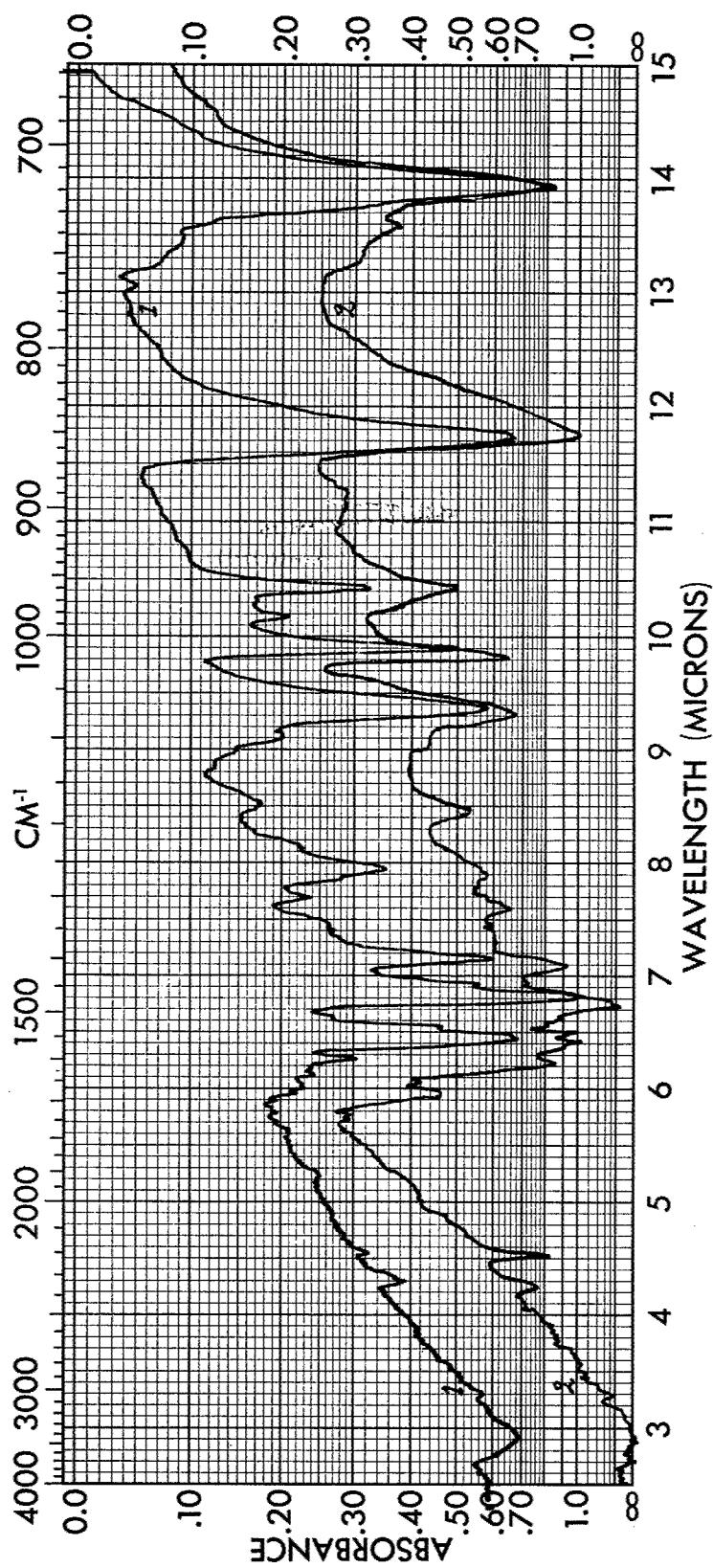


Figure 8. Infrared Spectra of 1: Residue of Poly-1,4-phenylene-2,5-(1,3,4-oxadiazole) at 350°C;
2: Residue at 450°C

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13. ABSTRACT Poly-1,3-phenylene hydrazide, when heated to 250°C in vacuum, partially undergoes cleavage of the N-N bond to yield isophthalonitrile, water, carbon monoxide, and carbon dioxide. The major part converts to the corresponding polyoxadiazole. Poly-1,3- and -1,4-phenylene -2,5,(1,3,4-oxadiazole) decompose essentially in the 450 to 500°C region to yield isophthalonitrile (also p-aminobenzonitrile in the case of the 1,4-polymer), nitrogen, carbon dioxide, hydrogen cyanide, carbon monoxide, water, ammonia, methane, and hydrogen. The 1,4-polymer decomposes at a slightly higher temperature than the 1,3-polymer and forms less gaseous products and more condensate. The oxadiazole ring degrades before the benzene ring. Initial competing reactions seem to be the removal of nitrogen and further degradation of the remaining ether linkage, and the elimination of oxygen with subsequent cleavage of the residual -C=N-N=C- linkage.		

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Polymer						
Polyhydrazide						
Polyoxadiazoles						